PTO 11-2391

Chinese Article
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UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. March 2011

Translated by: FLS, Inc.

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Source: Guangzhou Chemical Engineering, 2001, Vol. 29, No. 4, PP. 27 - 29

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Study on the Extractio of the Tea Polyphenol

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Abstract The operation parameters of extraction of tea polyphenol are studied in this paper. Especially the extraction and application are discussed in detail with supercritical carbon dioxide fluid. The best conditions for the extraction are obtained.

Keywords tea polyphenol, extraction, supercritical fluid, CO_2
Supported by the Guangzhou City Education and Scientific Research Fund

The abundant tea polyphenol found in tea leaves are the key physiologically active components for the pharmacological effect of tea leaves. Tea polyphenol (also referred to as TP) is not only a type of new natural antioxidant, but also provides significant anti-aging through pharmacological effects such as eliminating excessive free radicals; removing fat; reducing blood sugar, lipids, and cholesterol; preventing coronary heart disease; and inhibiting tumor cells. It is vital to food processing, pharmaceutical, and household chemical industries. In recent years, use of the extract of low-end tea leaves or waste from processing tea leaves to produce a high-value and fine chemical product - tea polyphenol - has become a topic of increasing interest to scientists and manufacturers. This article analyzes the properties of tea polyphenol and compares extraction methods. Through experimentation, research on the possibility of using supercritical extraction technologies to extract tea polyphenol and the optimal techniques and conditions are provided.

* Numbers in the margin indicate pagination in the foreign text.

1. Tea Polyphenol Composition and Properties

Tea polyphenol is the gross material of the polyphenol substance in tea leaves. It is a white indefinite powder that easily dissolves in water and can be dissolved in methanol, ethanol, acetone, and ethyl acetate, but does not dissolve in chloroform. The tea polyphenol content in green tea is quite high, occupying 15% to 30% of its mass. Tea polyphenol substances can generally be separated into six types: flavanols A, anthocyanins, flavonoids, flavonols B, and phenolic acids [translator's notes: only five types listed in source, with flavonols twice]. Thereof, flavanols A (primarily being catechin compounds) are the most important as they occupy 60% - 80% of the total tea polyphenol content. Next is flavonols B and the remaining phenol content is quite low.

Catechin compounds are a key ingredient in tea polyphenol. Their basic structure is a two-link (or adjacent) benzene phenol and pyran derivatives. This type of structure has adjacent phenol groups that provide antioxidant activity greater than typical non-phenol or single phenolic hydroxyl antioxidants. Tea polyphenol antioxidants extracted from tea leaves is such a catechin compound. Its antioxidant activity is better than butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and tertiary butylhydroquinone (TBHQ), and is safe and non-toxic.

2. Tea Polyphenol Extraction Methods

2.1. Organic Solvent Extraction Methods

This is currently one of the widely used methods within China. It principle rests on utilizing the difference of solubility of the different compounds in tea leaves in different solutions to provide extraction and isolation. Said method is quite simple and the extraction yield of tea polyphenol is 10% - 15%. However, the amount of organic solved used is great. Solvent recovery equipment and the amount of energy exhausted are quite extensive.

2.2. Ion Precipitate Extraction Method

Said method primarily utilizes certain metal ions capable of precipitating tea polyphenol which isolates it from caffeine. /28
The features of said method include using a reduced amount of organic and the tea polyphenol content of the obtained product is greater, reaching 95% or more. However, the steps to perform this technique are rather strict and there is abundant sludge as well as solutions that need to be processed afterward.

2.3. Absorption Separation Extraction Method

This method involves extraction by soaking green tea leaves (or tea dust) in hot water three times and combining the extraction solution. The tea leaf extract then passes through a high polymer absorbent where absorption occurs. It is then eluted using a 90% ethanol solution so that the absorbed tea polyphenol separates with the ethanol. Reduced pressure distillation is used to recover the ethanol. The solution is condensed and vacuum dry or spray dry to obtain tea polyphenol. The techniques and technology for said method

are simple and the amount of energy required is low. However, a high absorption absorbent with strong selectivity for tea polyphenol is required.

There are several extraction methods for tea polyphenol, but there are problems inherent to each one. Compared to typical extraction and isolation methods, supercritical fluid extraction techniques offer excellent transfer performance with stronger penetration strength and excellent selectivity. They provide greater solubility of organic solutions, offer a greater extraction yield, and result in good product quality while only needing warm conditions. They are especially useful for isolating thermal sensitive substances. At present, liquid CO_2 is commonly selected as the supercritical fluid because it is an inert solvent and the majority of it does not undergo a chemical reaction with the extract. It is also non-toxic and will not leave a residue in the extract. Its supercritical point is low ($Pc = 7.374 \times 10^4$ kPa, $Tc = 304.1$ K) and the technology of the equipment is easily satisfied. Moreover, the low operating temperature can ensure that the quality of the extract will not be affected. CO_2 is very inexpensive and easily obtained. The cost of using it is very low. Therefore, it was determined that supercritical CO_2 liquid extraction would be used to extract tea polyphenol from tea leaves. Because the solvent performance of CO_2 can be controlled by adjusting pressure and temperature, tea polyphenol extract can be obtained. Therefore, we probed the technical conditions of extracting

tea polyphenol with supercritical CO_2 to determine optimal extraction conditions.

3. Experimental Research on Extracting Tea Polyphenol with Supercritical Carbon Dioxide

3.1. Path of the Technique

This experiment utilizes the following path of technique: pre-process raw materials → extraction with supercritical carbon dioxide → isolation → product.

3.2. Experiment Equipment and Flow

The experiment for this research used 1L supercritical extraction devices from the Modern Chemical Engineering Key Laboratory of the Huanan College of Engineering. Said equipment and processes are as shown in Figure 1.

Within the diagram, the temperature of the extractor, separator, preheater, condenser, and CO_2 storage was controlled by a water bath. The pressure of the extractor and separator was controlled by a throttle valve. The flow rate was controlled by a CO_2 calculation pump. There are two separators.

3.3. Raw Materials and Reagents of the Experiment

Crude tea leaves

CO_2 extract, Guangzhou Nitrogen Factory, food grade, 99% or greater purity.

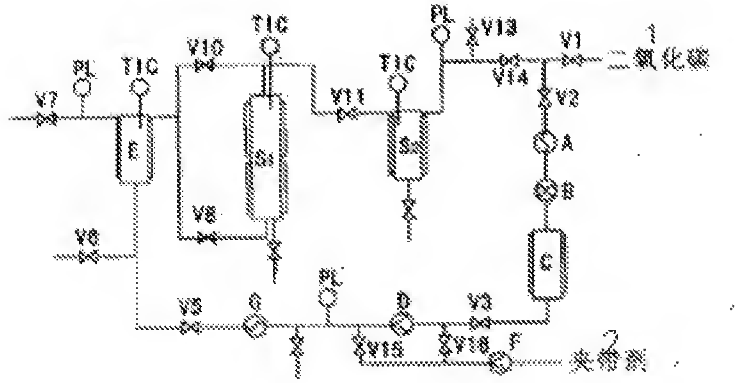

Figure 1. Supercritical CO_2 Extraction Equipment Flowchart
Key:
1. Carbon dioxide
2. Entrainer

A: Cold trap, B: flowmeter, C: storage, D: high-pressure pump, E: extraction container, F: entrainer pump, G: heat exchanger, S1: separator, S2: separator container, V1 - V6: high-pressure valve, TIC: temperature inducer, PL: pressure gauge

3.4. Experiment Tasks and Determination of Conditions

Based on the laboratory conditions, the highest extraction pressure selected was 25 MPa and the separation pressure was controlled to between 5 and 6 MPa. The extraction temperature selected was 50 °C and the separation temperature was 40 °C. Each batch of raw material was 100 g tea dust.

Considering that the dissolving process of CO_2 on substances is the mutual permeation and diffusion process between the CO_2 and the substance. The diffusion rate is related to the state of the system and the difference in concentration between the CO_2 and the substance. Under the conditions of this experiment, the state of the system is

defined. The difference in concentration is the key factor of what affects the diffusion rate. The greater the amount of CO_2 that flows, the greater the difference in concentration which provides increasing benefit for extraction. However, when the flow rate is greater than a certain value, the concentration difference is already very large, compared to the largest concentration of the flow not at maximum. At this time, it does not increase as the flow increases and there is signification change whereby a greater flow rate of liquid CO_2 causes the contact between the liquid CO_2 and the tea leaf dust to stop and reduce over time, which is not beneficial for extraction. Lower flow rates means extraction is not practical. The CO_2 flow rate needs to exist at a specific value. The CO_2 flow rate selected for this experiment was between 2 and 3 L/h.

The task of the experiment is to research the affect of extraction pressure and extraction time on the extraction rate under a certain extraction temperature.

3.5. Experiment Process

In order to find the optimal technical conditions of supercritical CO_2 liquid extraction of tea polyphenol, we performed a set of ten experiments based on the experiment task. Within the experiment, a fine grinder was used to grind the coarse tea leaves. 100 g of the processed tea leaves were weighed. This was packed into an extraction vat. The extractions were performed separately under selected conditions. 0.5 hours after the extraction circulation

starts, the valve at the bottom of the separator could be opened at regular intervals to release the extraction solution. This was weighed and measured. The experiment was stopped after a predetermined circulation extraction time had passed.

3.6. Evaluation Method for the Effectiveness of the Experiment

The GB8317-87 standard (1) can be used to assess the tea polyphenol content.

3.7 Experiment Results and Discussion

See Table 1 for the results of the experiment. /29

Table 1. Extraction Conditions and Results

	1 萃取压力 (MPa)	2 萃取温度 (℃)	3 分离压力 (MPa)	4 分离温度 (℃)	5 萃取时间 (h)	6 流量 (L/h)	7 剩余物 (g)	8 萃取率 (%)
1	10	50	5.0	40	3	2.0	92.8	7.2
2	15	50	5.0	40	3	3.0	92.5	7.5
3	20	50	5.0	40	3	2.5	91.8	8.2
4	22	50	5.6	40	3	2.4	91.0	9.0
5	25	50	6.0	40	3	2.5	90.6	9.4
6	20	50	6.0	40	1	2.6	93.0	7.0
7	20	50	5.8	40	2	2.0	92.8	7.2
8	20	50	5.7	40	3	2.2	91.7	8.3
9	20	50	6.0	40	4	2.0	91.3	8.7
10	20	50	6.0	40	5	2.2	91.0	9.0

Key:
1. Extraction pressure (MPa)
2. Extraction temperature (°C)
3. Separation pressure (MPa)
4. Separation temperature (°C)
5. Extraction time (h)
6. Flow rate (L/h)
7. Remainder (g)
8. Extraction rate (%)

3.7.1. The Effect of Extraction Pressure

From Table 1 it can be seen that as the extraction pressure increases, the extraction rate increases significantly. Figure 2 below is obtained with the extraction pressure on the X-axis and the extraction rate on the Y-axis:

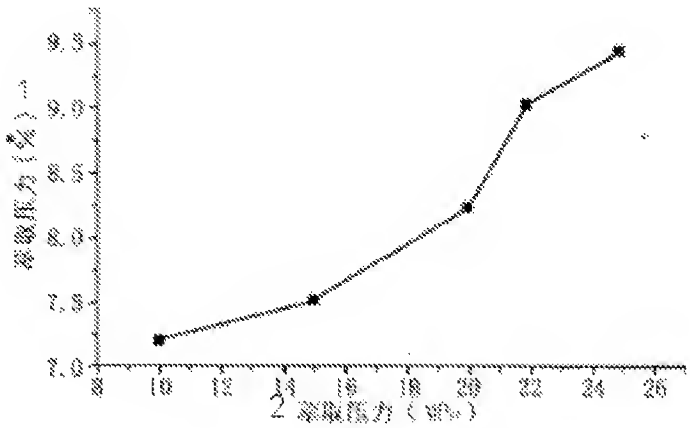

Figure 2. The relationship between extraction pressure and extraction rate.

Key:
1. Extraction pressure (%) [translator's note: likely a typo]
2. Extraction pressure (MPa)

Figure 2 shows: when the extraction pressure increases from 20 MPa to 22 MPa, the slope of the curve is at its greatest where the extraction rate increases from 8.2% to 9.0%. Compared to the rest of the curve, this increase is particularly large. The overall trend of the curve is an increasing state, which means as the extraction pressure increases, the extraction rate continually increases. This is because the solubility of tea polyphenol in CO_2 increases as the pressure increases.

3.7.2. The Effect of Extraction Time

Figure 3 is obtained with the extraction time as the X-axis and the extraction rate as the Y-axis. From this diagram, it can be seen that the slope of the curve is greatest at the section when the extraction time increases from 2 hours to 3 hours. At this time, the extraction rate increases from 7.2% to 8.3%, or an increase of 1.1%. Under these conditions, the effect of extraction time on extraction rate is not clear. The increasing trend of the curve is not large, which is in part due to the lower extraction pressure.

Under normal circumstances, the longer the extraction time, the greater the extraction rate.

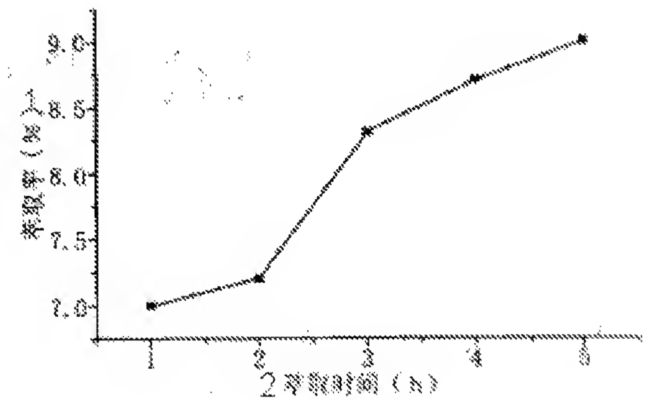

Figure 3. Graph of the relationship between extraction time and extraction rate.

Key:
1. Extraction rate (%)
2. Extraction time (h)

Due to the fact that as the extraction time increases, the transfer of mass of the supercritical CO_2 and tea polyphenol gradually reaches an optimal state and thus the extraction rate increases. However, if the extraction time is too long, the overall extraction rate

decreases to the point where it is not economical. In addition, long extraction times mean a large amount of kinetic energy. The amount of wear a machine can withstand is limited, so an extraction time of 5 hours is suitable.

4. Conclusion

Use of supercritical CO_2 for the extraction of tea polyphenol in tea leaves is completely achievable. Suitable experimental conditions for using supercritical CO_2 to extract tea polyphenol from tea leaves are: an extraction pressure of 20 MPa, an extraction temperature of 50°C, a separation pressure of 5 MPa, a separation temperature of 40°C, a CO_2 flow rate of 2.5 L/h, and an extraction time of 5 h. Under these conditions, the extraction rate of tea polyphenol can reach 9.0%.

Compared to traditional organic solvent extraction methods, supercritical CO_2 extraction utilizes CO_2 as the extraction solvent where the product does not contain any residual chemical solvents, thus maintaining the natural purity of the product. The temperature of the extraction is near room temperature and thus there are no thermal sensitivity issues that need to be resolved. The product also will not easily oxidize, resulting in a high quality product.

During the extraction process, there are no toxic substances to release and no issues with relation to polluting the environment. This follows the developing trend in “green chemistry” and offers a promising trend in the extraction of tea polyphenol.

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